



# Monodisperse SnO<sub>2</sub> anchored reduced graphene oxide nanocomposites as negative electrode with high rate capability and long cyclability for lithium-ion batteries

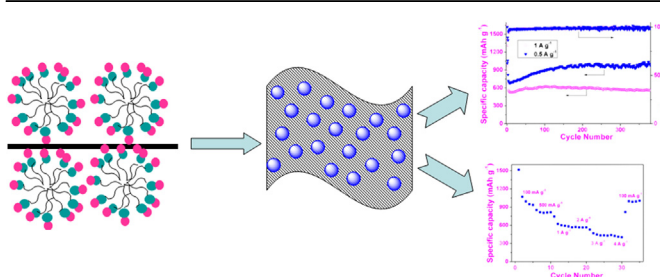
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## HIGHLIGHTS

- Monodisperse SnO<sub>2</sub> anchored rGO composite is synthesized as anode materials.
- Aided with SDS, SnO<sub>2</sub> nanocrystal is dispersed on rGO sheets uniformly and tightly.
- Urea is used to control the precipitation of SnO<sub>2</sub> and reduce GO into rGO.
- The sample shows high capacity, excellent rate capability and cyclic performance.
- TEM images in different charge–discharge cycles reveal the electrode evolution.

## GRAPHICAL ABSTRACT



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## ABSTRACT

In this manuscript, we present a facile and friendly wet chemical method to prepare monodisperse SnO<sub>2</sub> nanocrystals assembled on reduced graphene oxide (RGO). Aided with sodium dodecyl sulfonate, small SnO<sub>2</sub> nanoparticles (~5 nm) are deposited onto the flexible support evenly and tightly. A cheap compound, urea, is used for the controlled precipitation of SnO<sub>2</sub> and the reduction of graphene oxide. When tested as the anode material, the hybrid composite electrode delivers excellent cyclability at high current density, such as high reversible capacity over 1000 mAh g<sup>-1</sup> after 400 cycles at 0.5 A g<sup>-1</sup> and ~560 mAh g<sup>-1</sup> after 400 cycles at 1 A g<sup>-1</sup>. The composites also exhibit superior rate capability varying from 0.1 to 4 A g<sup>-1</sup>, and possess capacity of 423 mAh g<sup>-1</sup> at 4 A g<sup>-1</sup>. This synthesis strategy seems to be suitable for industrial production and can also be extended to produce a variety of metal oxide/RGO composites.

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## 1. Introduction

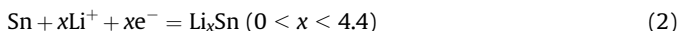
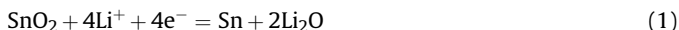
Since their first commercialization about 20 years ago, rechargeable lithium-ion batteries (LIBs) have become the

dominant power sources for portable electronic devices, due to their high energy density, fast charge/discharge rate, light weight, and long cycle life. However, the conventional graphite anode, which is limited by its low theoretical capacity of 372 mAh g<sup>-1</sup>, poor rate capability, and security issue originated from lithium dendrite, cannot fulfill the growing demands for high performance LIBs, especially for the applications in electric vehicles and hybrid electric vehicles [1,2]. Therefore, exploration of the next-generation

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anode materials with high capacity, excellent rate capability, and high safety has been put on the schedule. For instance, tin oxide ( $\text{SnO}_2$ ) has received special attention, since it is expected to deliver a high theoretical capacity. It is believed that, two principal electrochemical processes including conversion and alloy mechanisms are involved in the  $\text{SnO}_2$ -based anode:



Normally, the conversion process of Eq. (1) is thought to be electrochemically irreversible and has no contribution to the reversible capacity, so the theoretical capacity of  $\text{SnO}_2$  is calculated to be  $790 \text{ mAh g}^{-1}$  based on the highly reversible alloy reaction of Eq. (2) [3–6]. Recently, the fully/partially reversible conversion reaction of Eq. (1) has been observed in some nanosized  $\text{SnO}_2$ -based anodes [7–10] and the theoretical capacity of  $\text{SnO}_2$  can be extended to  $1490 \text{ mAh g}^{-1}$  accordingly. Unfortunately, the commercialization of  $\text{SnO}_2$  anodes for LIBs is still largely hampered by their serious capacity fading upon cycling and/or poor rate capability, mainly ascribing to the large volume changes ( $\sim 300\%$ ) upon  $\text{Li}^+$  insertion/extraction [11–14].

To circumvent these issues, various  $\text{SnO}_2$  nanostructures have been designed and constructed to improve their electrochemical performance, such as hollow nanostructures [5,15–17], hybrid  $\text{Fe}_2\text{O}_3/\text{SnO}_2$  nanorattles [18], nanosheets [4,19], nanoboxes [20], nanotubes [21,22], nanowires [23,24], and nanospheres [25].  $\text{SnO}_2$  has also been incorporated with carbon to prepare  $\text{SnO}_2$ -C hybrid electrode materials [26–41], because carbon can not only alleviate the volume change but also result in good electrical contact and enhanced pathways for electronic transport kinetics. Among them, graphene oxide (GO), especially reduced graphene oxide (rGO), has been investigated extensively due to its high surface area, superior electronic conductivity, and excellent mechanical flexibility [5,7,27,32–41]. However, these synthesis processes are commonly time and energy consuming, and associated with complicated and rigorous conditions.

In this work, a facile wet chemical method is employed to synthesize monodisperse  $\text{SnO}_2$ /rGO composites (M-SGCs) as schematically illustrated in Fig. 1. Here, urea is used to control the release rate of  $\text{NH}_3$ , which promotes the reduction of GO into rGO and precipitates  $\text{SnO}_2$  nanoparticles mildly [42]. Sodium dodecyl sulfonate (SDS) plays the key role to anchor  $\text{SnO}_2$  nanocrystals on the rGO sheets tightly and insures their even distribution. The resultant M-SGCs that benefit from the highly active monodisperse  $\text{SnO}_2$  nanoparticles ( $\sim 5 \text{ nm}$ ), the flexible mechanical support of

rGO sheets, and unhindered electron flow between  $\text{SnO}_2$  and rGO, exhibit excellent cyclability at high current density and superior rate capability when tested as anode materials for LIBs.

## 2. Experimental

### 2.1. Sample preparation

All reactants are of analytical grade and used as purchased without further purification. GO sheets are first synthesized following a modified Hummers method described elsewhere [43]. In the typical synthesis route of M-SGCs,  $0.25 \text{ g}$  SDS is dissolved in  $7 \text{ mL}$  GO dispersion ( $10 \text{ mg mL}^{-1}$ ) under magnetic stirring. The mixture is diluted to  $30 \text{ mL}$  and sonicated for  $15 \text{ min}$  and then is added into a  $10 \text{ mL}$  portion of  $0.12 \text{ M}$   $\text{SnCl}_4$  in  $3.8 \text{ wt\%}$  HCl solution. After  $4.8 \text{ mL}$  of  $1 \text{ M}$  urea is added dropwise, the mixture is diluted to  $100 \text{ mL}$  and is further refluxed at  $90^\circ\text{C}$  in a sealed round bottom flask for  $16 \text{ h}$ . The obtained precipitate is washed with water thoroughly to remove the residual SDS and then dried at  $40^\circ\text{C}$  in vacuum. Finally, the sample is sintered at  $450^\circ\text{C}$  under an argon atmosphere for  $3 \text{ h}$  with a heating rate of  $2^\circ\text{C min}^{-1}$  to obtain the M-SGCs.

### 2.2. Materials characterization

The samples are characterized with X-ray powder diffraction (XRD) by a Philips X'-pert X-ray diffractometer with  $\text{Cu K}\alpha$  radiation ( $\lambda = 0.154056 \text{ nm}$ ). Raman spectroscopy is obtained in the confocal microprobe Raman system (LabRam-010,  $632 \text{ nm}$  as excitation source). Fourier transform infrared (FTIR) spectra are recorded with FTIR analyzer (Nicolet Magna-IR750). The thermogravimetric (TG) analysis is measured with TG2091F from room temperature to  $800^\circ\text{C}$  with a heating rate of  $10^\circ\text{C min}^{-1}$  in air. Scanning electron microscope (SEM) is obtained with a JEOL JSM-7500F scanning electron microscope. Transmission electron micrographs (TEM) analysis is performed with FEI TECNAI F30.

The electrochemical tests are carried out with the CR2016-type coin cell. Metallic lithium sheet is used as negative electrodes. The working electrode is fabricated by compressing a mixture of M-SGCs, conductive material (acetylene black) and binder polyvinylidene fluoride (PVDF) in a weight ratio of  $8:1:1$  onto a copper foil. The electrode is dried at  $120^\circ\text{C}$  for  $24 \text{ h}$  in vacuum oven and the cell assembly is operated in a glove box filled with pure argon. The Clegard 2300 microporous film is used as the separator. The electrolyte solution is  $1 \text{ M}$   $\text{LiPF}_6$  dissolved in a mixture of ethylene carbonate (EC)/dimethyl carbonate (DMC)/ethyl methyl carbonate (EMC) ( $1:1:1$  in volume) (Zhangjiagang, China). Charge–discharge experiments are performed between  $3$  and  $0.01 \text{ V}$  with the LAND CT2001A Battery Cycler (Wuhan China). Cyclic voltammetry (CV) measurements are characterized using a three-electrode cell and metallic lithium is used as the counter and reference electrode. The experiments are performed on CHI660A (CH Instruments, China) over the potential range from  $0.01$  to  $2.0 \text{ V}$  vs.  $\text{Li}^+/\text{Li}$  at a scan rate of  $0.1 \text{ mV s}^{-1}$ .

## 3. Results and discussion

The overall synthetic solution of M-SGCs is illustrated in Fig. 1. Firstly, a certain concentration of SDS molecules in aqueous solution tends to form micelle with the hydrophilic ends outside [44]. After the addition of  $\text{Sn}^{4+}$ , SDS $^-$  absorbs  $\text{Sn}^{4+}$  cations using its naked anion. Then the micelles with highly positively charged  $\text{Sn}^{4+}$  anchor tightly onto the surface of GO sheets through the strong electrostatic interaction, which are negatively charged under aqueous solution. On the other hand, the repulsive force between

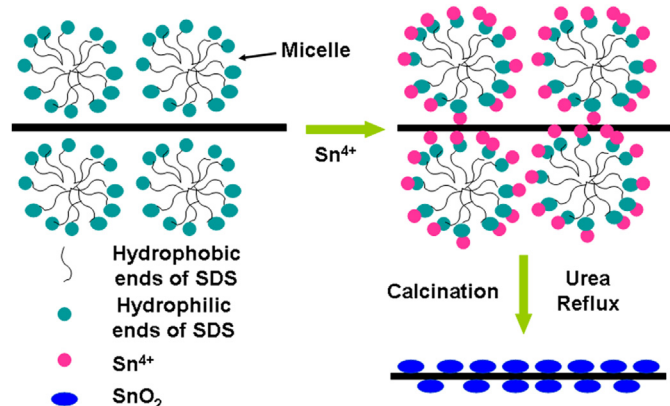


Fig. 1. Schematic diagram for the synthesis route of M-SGCs.

the micelles guarantees their uniformly monodispersion on the sheets surface. Subsequently, the released  $\text{NH}_3$  during the reflux step transforms  $\text{Sn}^{4+}$  into the  $\text{SnO}_2$  nanoparticles. Simultaneously, GO is reduced to rGO. After calcination, the final M-SGCs are obtained.

The crystal structure of M-SGCs is characterized with powder XRD and shown in Fig. 2a. All the diffraction peaks in the M-SGCs are assigned to a tetragonal phase  $\text{SnO}_2$  with space group  $P42_1nm$ . (JCPDS card no. 41–1445). There is no other impurity peaks observed, indicating the high phase purity of the product. The good crystallization is proved by the intense and sharp reflection peaks. Calculated from the broaden peak of (110) with Debye–Scherrer equation, the mean particle size of  $\text{SnO}_2$  in M-SGCs is evaluated to be about 5.2 nm. Interestingly, the peak of rGO in the composite is not observed. As shown in Fig. 2a, the rGO sheets show the typical peak centered at  $2\theta$  of  $24.6^\circ$ , indicating its successful reduction. However, the diffraction density of pure rGO is much lower compared with that of  $\text{SnO}_2$ , and the peak position of rGO ( $24.6^\circ$ ) is close to the (110) peak of  $\text{SnO}_2$  ( $26.5^\circ$ ) (see supporting information Fig. S1). So the peak of rGO and (110) peak of  $\text{SnO}_2$  are overlapped in the XRD pattern of the composite (see supporting information Fig. S2), thus inducing the absence of rGO peak.

The structure of M-SGCs is also investigated with Raman spectroscopy. As is shown in Fig. 2b, the Raman spectrum of GO shows two characteristic peaks located at about  $1330\text{ cm}^{-1}$  (D band, corresponding to  $\kappa$ -point phonons of  $A_{1g}$  symmetry) and  $1590\text{ cm}^{-1}$  (G band, corresponding to an  $E_{2g}$  phonon of  $\text{sp}^2$ -bonded carbon atoms). In the Raman spectrum of M-SGCs, the characteristic peaks of D band and G band for GO are observed at about  $1325$  and  $1590\text{ cm}^{-1}$ , respectively. The peaks located at about  $620$  and  $775\text{ cm}^{-1}$ , corresponding to the expansion and contraction vibration modes of Sn–O bonds in tetragonal  $\text{SnO}_2$ , should be assigned to the  $A_{1g}$  and  $B_{2g}$  symmetry of  $\text{SnO}_2$  [45]. This result confirms the presence of  $\text{SnO}_2$  in the composites. It is generally accepted that the

intensity ratio of the D to G band ( $I_D:I_G$ ) can reflect the disorder and defects of carbonaceous materials [46–48]. The  $I_D:I_G$  of M-SGCs is calculated to be 1.09, which is higher than that of GO (0.95). It should be ascribed to the reduction of GO into rGO by urea [42,48].

The formation of M-SGCs and the reduction of the GO in the composites are further confirmed with FTIR techniques. As is shown in Fig. 2c, the characteristic FTIR bands of GO are centered at  $1720$ ,  $1625$ ,  $1579$ ,  $1399$ ,  $1223$ , and  $1050\text{ cm}^{-1}$ , corresponding to the stretching vibration of C=O (carboxyl), C–O (epoxy), skeletal ring vibrations, O–H (carboxyl), C–OH (hydroxyl), and C–O (carboxyl or alkoxy), respectively [34,37]. In the FTIR spectrum of M-SGCs, no characteristic peaks of SDS are observed. In comparison with the spectrum of GO, the peaks related to C=O, C–O, and O–H bands are absent, suggesting the removal of most oxygen functionalities and the reduction of GO. The presence of the intense bands located at  $1567\text{ cm}^{-1}$ , where the C=C stretching vibration of benzene usually appears, indicates the healing of the basal structure of the graphite domains. The intense bands at around  $630\text{ cm}^{-1}$  observed in the M-SGCs should be assigned to the asymmetric and symmetric vibrations of Sn–O–Sn, confirming the formation of the M-SGCs. As is shown in TG curve (Fig. 2d), the weight loss of 34% implies that the weight portion of  $\text{SnO}_2$  is higher than 60% in the composite.

The morphology of the resultant M-SGCs is examined with SEM and TEM measurements and is shown in Fig. 3. As shown in the SEM image (Fig. 3a), M-SGCs show crumpled layer structures, consisting of various rGO sheets arranged in a disordered manner. The bright area reveals the dense regions of  $\text{SnO}_2$  nanocrystals [49,50]. The TEM images (Fig. 3b, c) reveal that monodisperse nanocrystals are homogeneously distributed on the rGO sheets. The average particle size of  $\text{SnO}_2$  nanocrystals extracted from these images is about  $\sim 5\text{ nm}$ , which is in good agreement with the XRD results. In contrast with it, the TEM image (Fig. 3d) of  $\text{SnO}_2$ –rGO hybrid composites (SGCs), which is synthesized without SDS, shows uneven dispersion of  $\text{SnO}_2$  particles on rGO layer. In one

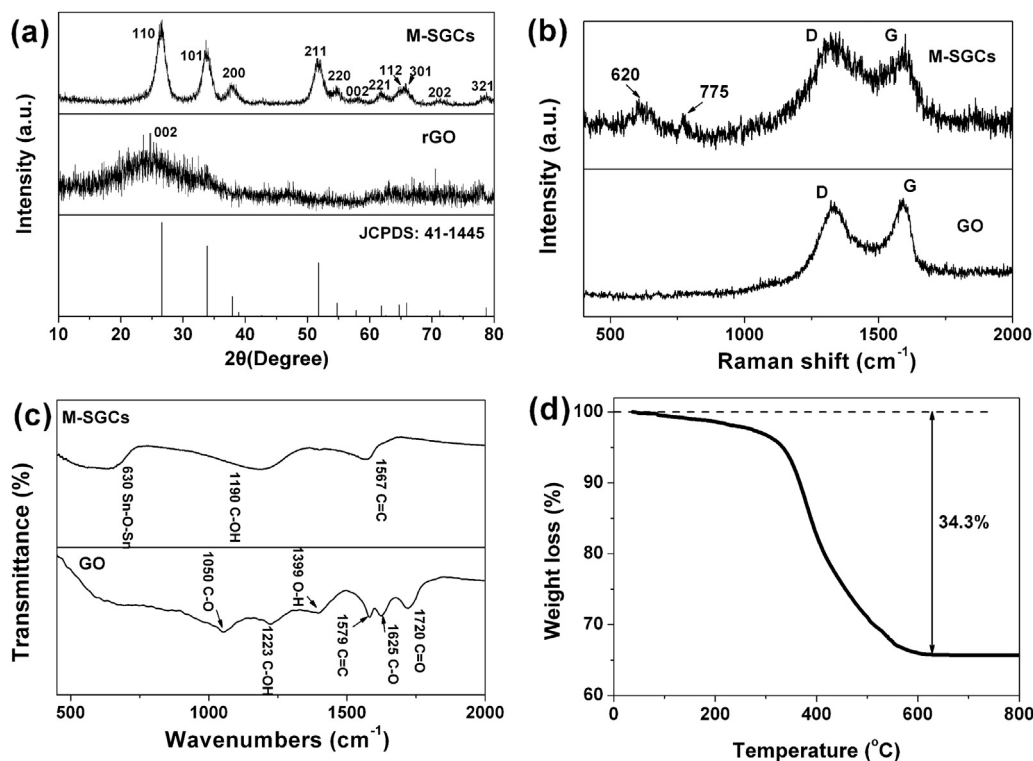


Fig. 2. (a) XRD patterns of as-prepared M-SGCs and rGO. (b) Raman spectra and (c) FTIR spectra of M-SGCs and GO. (d) TG curve of M-SGCs.



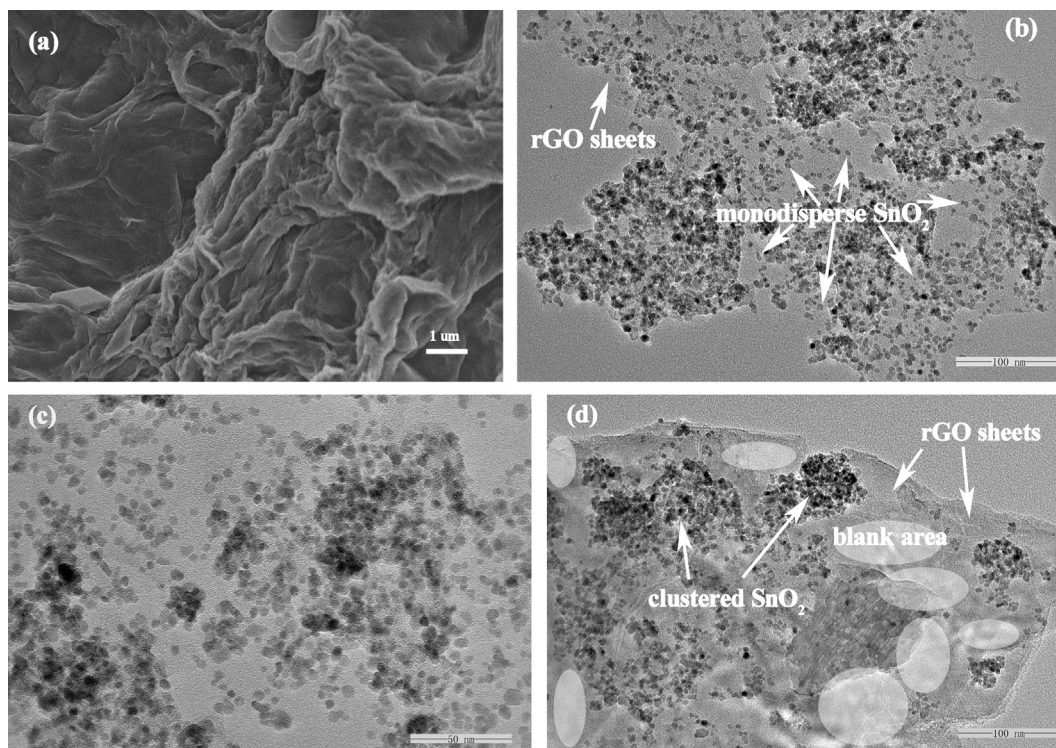


Fig. 3. (a) SEM and (b, c) TEM images of M-SGCs. (d) TEM image of SGCs.

hand, part of rGO sheet surface is blank without the distribution of  $\text{SnO}_2$ . On the other hand, clustered nanocrystals are observed in certain areas. This result suggests that the addition of SDS is beneficial for the monodispersed distribution of  $\text{SnO}_2$  nanocrystals.

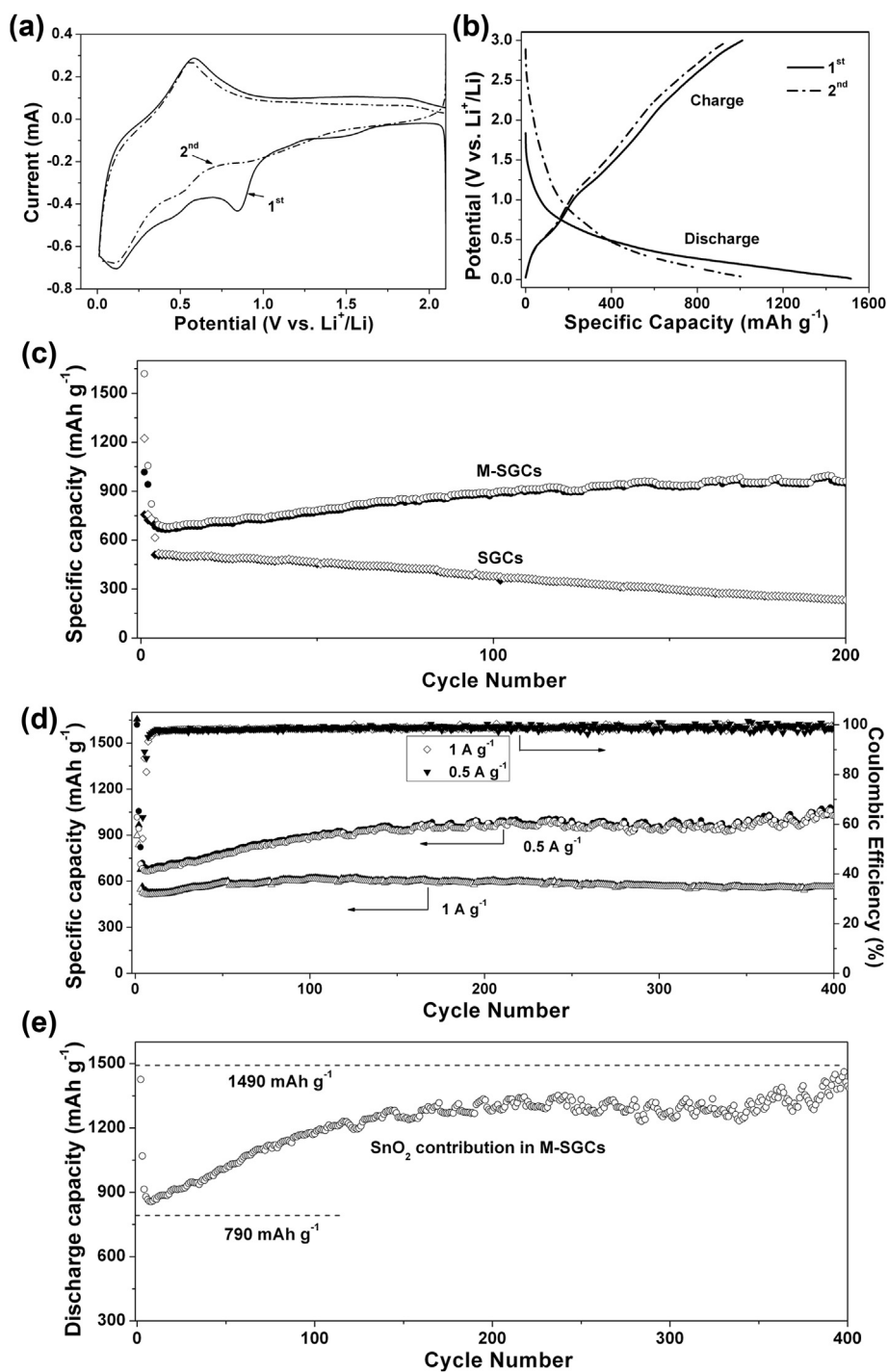
The  $\text{Li}^+$  storage properties of the obtained M-SGCs are investigated as anode materials for LIBs with the laboratory  $\text{Li}^+$  half-cell configuration. Fig. 4a presents the CV curves of M-SGCs at a scan rate of  $0.1 \text{ mV s}^{-1}$  between 0.01 and 2 V vs.  $\text{Li}^+/\text{Li}$ . In the first cycle, two sharp cathodic peaks at 0.85 and 0.12 V can be ascribed to the formation of  $\text{Li}_2\text{O}$  and the lithium alloying reaction with Sn, respectively [36,51]. And the small cathodic peak at 0.46 V is related to the decomposition of the electrolyte on the surface of the  $\text{SnO}_2$  nanoparticles and rGO in the formation process of solid electrolyte interface (SEI) layer [7,32,52]. In addition, the anodic peaks at around 0.58 V and 1.3 V can be assigned to the de-alloying of  $\text{Li}_x\text{Sn}$  and  $\text{Li}_2\text{O}$  to  $\text{SnO}_2$ , respectively [7–9]. The latter oxidation peak (1.3 V) strongly indicates that the conversion reaction of Eq. (1) takes place reversibly during the charge/discharge process of M-SGCs anode. The corresponding slopes and plateau also exist in the 1st and 2nd galvanostatic charge–discharge profiles of M-SGCs electrode (Fig. 4b). It can be clearly observed that, M-SGCs show a first discharge capacity of  $1515 \text{ mAh g}^{-1}$  and a charge capacity of  $1010 \text{ mAh g}^{-1}$  at a current density of  $100 \text{ mA g}^{-1}$ . The relatively low coulombic efficiency (about 67%) in the first cycle is ascribed to the irreversible formation of amorphous lithium oxide and the decomposition of electrolyte and lithium salt in the formation of SEI layer.

The cyclic performances of the M-SGCs and SGCs electrodes at a relatively high current density of  $0.5 \text{ A g}^{-1}$  are shown in Fig. 4c. The discharge capacities of SGCs fade dramatically from 754 (the second cycle) to  $233 \text{ mAh g}^{-1}$  in the 200th cycle, delivering poor capacity retention of 31%. In comparison, the discharge capacities of M-SGCs electrode decrease slightly from 1057 (the second cycle) to  $961 \text{ mAh g}^{-1}$  in the 200th cycle, showing higher capacity retention of 91%. Furthermore, it exhibits a comparatively high capacity of

$1036 \text{ mAh g}^{-1}$  with the capacity retention of 98% in the 400th cycle (shown below in Fig. 4d). It can be clearly observed that the M-SGCs electrode exhibits improved cyclic stability than that of SGCs electrode, which should be attributed to the monodispersion of  $\text{SnO}_2$  nanoparticles in the M-SGCs achieved with the aid of SDS.

With the aim to further explore the high rate capability of M-SGCs anode, the cyclic performance at high current densities of 0.5 and  $1 \text{ A g}^{-1}$  are tested, respectively. As is shown in Fig. 4d, M-SGCs anode delivers an excellent cyclic performance at  $0.5 \text{ A g}^{-1}$ . After initial several conditioning cycles, its discharge capacity shows obvious increase. The stable capacity over  $790 \text{ mAh g}^{-1}$  (theoretical capacity based on an alloy mechanism) is obtained after 53 cycles and reaches  $1036 \text{ mAh g}^{-1}$  in the 400th cycle. This interesting capacity increase should be assigned to the contribution of the improved conversion reaction ( $\text{SnO}_2 + 4\text{Li}^+ + 4\text{e}^- = \text{Sn} + 2\text{Li}_2\text{O}$ ). With the increasing electrochemical cycles, the pulverization of electrode materials will make the in-situ formed Sn nanoparticles smaller and smaller. It is believed that, the decrease of reagent particle size could reduce the activation energy for solid-state double decomposition reactions, thus boosting the conversion reaction and contributing to the reversible capacity. And the excellent cyclic performance is also observed at higher current density of  $1 \text{ A g}^{-1}$ . M-SGCs deliver superior cyclic capability over  $560 \text{ mAh g}^{-1}$  for a long life beyond 400 cycles. In the meanwhile, the M-SGCs anode shows excellent coulombic efficiency at both the current densities. The M-SGCs show initial coulombic efficiencies of 63 and 54% at 0.5 and  $1 \text{ A g}^{-1}$ , respectively. After several cycles, both the coulombic efficiencies reach up and maintain higher than 98% throughout the 400 cycles. Thus, it can be concluded that the M-SGCs electrode delivers a superior cycling performance as well as high coulombic efficiency at high rate charge/discharge process.

It is worth noting that the specific capacity values are estimated based on the total mass of the M-SGCs. In order to evaluate the contribution of  $\text{SnO}_2$  in the M-SGCs, the discharge capacities at  $0.5 \text{ A g}^{-1}$  are calculated based on the mass of  $\text{SnO}_2$  (66%). The weight



**Fig. 4.** (a) Cyclic voltammogram of the M-SGCs electrode at the scanning rate of  $0.1 \text{ mV s}^{-1}$ . (b) The discharge–charge profiles of M-SGCs at the current density of  $100 \text{ mA g}^{-1}$ . (c) Cyclic performance of M-SGCs and SGCs at  $0.5 \text{ A g}^{-1}$ . (d) Cyclic performance of M-SGCs at  $0.5 \text{ A g}^{-1}$  and  $1 \text{ A g}^{-1}$  after 2 cycles at  $100 \text{ mA g}^{-1}$ . (e) Discharge capacities versus cycle numbers of  $\text{SnO}_2$  in the M-SGCs.

content of rGO in M-SGCs is 34% based on the TG measurements (Fig. 2d). The capacity of  $\text{SnO}_2$  in the hybrid material is calculated as follows:  $C_{\text{SnO}_2} = (C_{\text{M-SGCs}} - C_{\text{rGO}} \times 34\%) / 66\%$ . The rGO delivers a specific capacity of  $\sim 340 \text{ mAh g}^{-1}$  (see supporting information Fig. S3). As is shown in Fig. 4e, the second discharge capacity of  $\text{SnO}_2$  is  $1425 \text{ mAh g}^{-1}$ , which is much higher than the theoretical capacity of  $790 \text{ mAh g}^{-1}$  (based on the alloy reaction process) and is very close to the theoretical value of  $1490 \text{ mAh g}^{-1}$  (based on both the conversion and the alloy processes). Moreover, the capacity of  $\text{SnO}_2$

in the composites is always higher than  $790 \text{ mAh g}^{-1}$ , as it can be clearly observed in Fig. 4e. After 400 cycles, the  $\text{SnO}_2$  in the M-SGCs delivers a high capacity of  $1394 \text{ mAh g}^{-1}$ , indicating superior capacity retention of 98%. Thus, the completely reversible electrochemical conversion between  $\text{SnO}_2$  and  $\text{Li}_{4.4}\text{Sn}$  has been successfully demonstrated in our presented M-SGCs anode. To our best knowledge, the M-SGCs presented here is among the best to prove the highly reversible reaction of  $\text{SnO}_2$ -based anode with a long cyclic life up to hundreds of cycles [7,8].

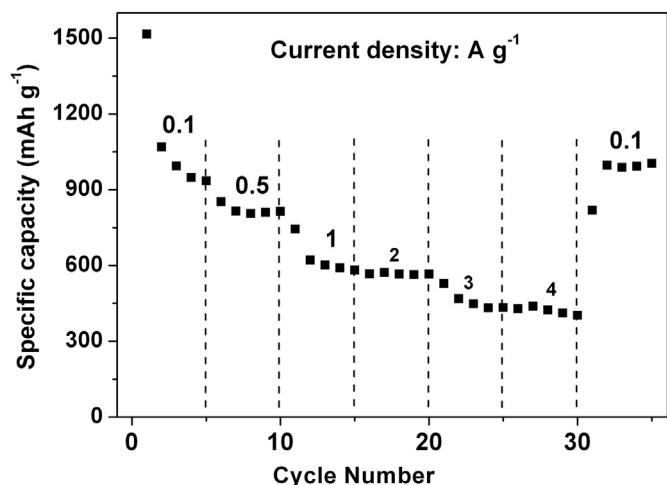


Fig. 5. Rate capability of M-SGCs electrode.

The excellent rate performance of M-SGCs is also observed due to the hybrid benefits of proper chemical components and nano-structures. As shown in Fig. 5, the M-SGCs electrode exhibits superior rate performance when the current densities vary from 0.1, 0.5,

1, 2, 3–4  $\text{A g}^{-1}$ . The capacity values can retain as high as 572 and 423  $\text{mAh g}^{-1}$  at rates of 2 and 4  $\text{A g}^{-1}$ , respectively. Remarkably, after this rigorous test process, the M-SGCs anode can recover to its initial value of 1004  $\text{mAh g}^{-1}$  when the current density returns to 0.1  $\text{A g}^{-1}$ , exhibiting good capacity retention ability.

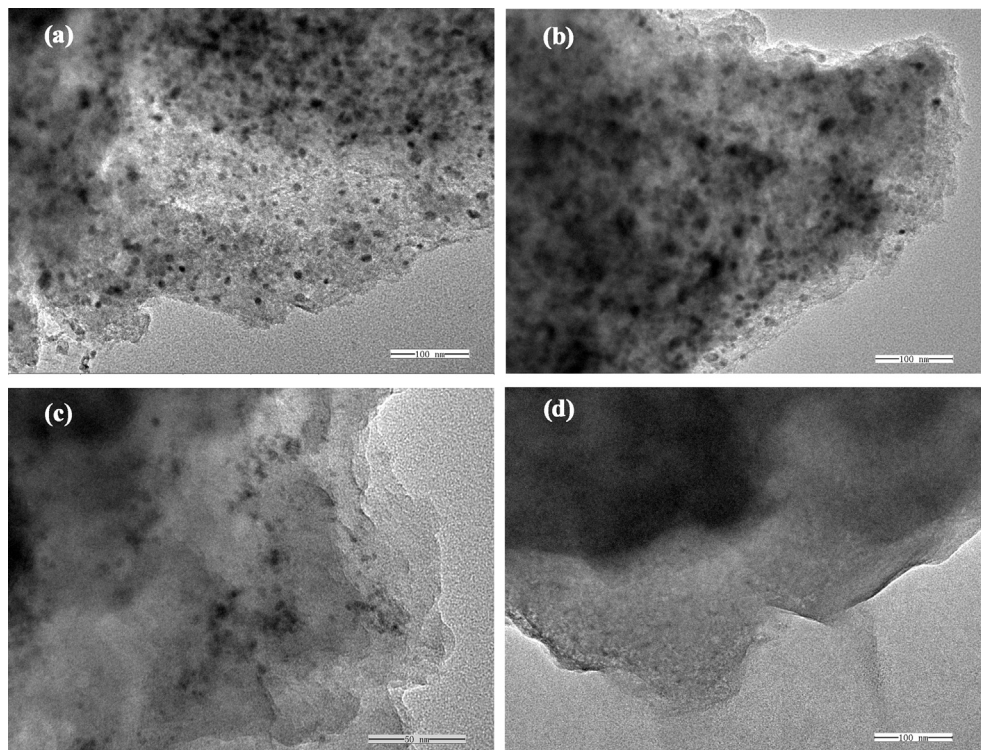
The superior electrochemical performance of the M-SGCs anode is compared with the data that have been reported recently in Table 1. These data about the  $\text{Li}^+$  storage properties of  $\text{SnO}_2$ -based materials mainly focus on their long life cycles ( $\geq 50$  cycles) performance as the anode. It is shown that  $\text{SnO}_2$ /graphene composites presented by Lin et al. exhibit high capacity at high rate of 2  $\text{A g}^{-1}$  [40], which is similar to the value of the M-SGCs. But its reversible capacity and cycling life obtained at lower discharge rate is inferior to those of M-SGCs. The M-SGCs also exhibit better electrochemical performance than the data that have been marked in Ref. [8,9,33,38,39], which are the exciting results for  $\text{SnO}_2$ -based anode that have been presented recently. Zhou et al. have reported the highest capacity that has been reported for  $\text{SnO}_2$  anode materials [7]. The presented M-SGCs exhibit comparable capacity and cyclic stability to the data at rate of 0.5  $\text{A g}^{-1}$  in [7]. Although they obtain slightly higher reversible capacity at higher rate of 1  $\text{A g}^{-1}$ , the corresponding cyclic performance is absent. However, the M-SGCs anode delivers outstanding cycling stability (567  $\text{mAh g}^{-1}$  at 400 cycles) at 1  $\text{A g}^{-1}$ . Thus, the electrochemical performance of the

Table 1

Comparison of the electrochemical performance of the M-SGCs electrode with those of  $\text{SnO}_2$  based electrodes reported in the literature.

Samples	Synthesis method	Current rate (mA g <sup>-1</sup> )	Discharge capacity (mAh g <sup>-1</sup> )	Capacity retention (mAh g <sup>-1</sup> )/(cycles)	Ref./publication year	
M-SCGs	Reflux	500	1057 (2nd)	1036/400	Present work	
		1000	968 (2nd)	567/400		
		2000	571			
		3000	528			
		4000	439			
SnO <sub>2</sub> /Cu	Hydrothermal	200	713	535/150	[41]/2013	
SnO <sub>2</sub> /graphene		100	1130	825/50	[40]/2013	
SnO <sub>2</sub> /graphene		2000	580			
		100		800/200	[39]/2013	
		1000		600/50		
SnO <sub>2</sub> /graphene		2000		400/100		
		100	931	718/200	[38]/2013	
		500		514/200		
SnO <sub>2</sub> /graphene		Hydrothermal	~ 78		847/50	[37]/2013
SnO <sub>2</sub> /graphene		Hydrothermal	100	907	710/50	[36]/2012
SnO <sub>2</sub> /graphene	Hydrothermal	200	659	575/50		
		3200		380/50	[35]/2012	
		100	950	775/50	[34]/2011	
SnO <sub>2</sub> /graphene	Reflux	100		872/200	[33]/2013	
SnO <sub>2</sub> /graphene	Hydrothermal	50		910/50	[32]/2012	
SnO <sub>2</sub> /carbon nanofiber		100		383/30	[31]/2012	
SnO <sub>2</sub> /CNT		25		650/100	[30]/2012	
SnO <sub>2</sub> /CNT		200		497/300	[29]/2011	
SnO <sub>2</sub> /graphene		400		518/50	[28]/2011	
SnO <sub>2</sub> /graphene		50	1080	649/30	[27]/2011	
SnO <sub>2</sub> /graphene		Hydrothermal	~ 156	786	558/50	[26]/2010
SnO <sub>2</sub> nanorod array		Solvothermal	7820	720	590/20	[24]/2013
CNT@SnO <sub>2</sub> nanotube			~ 390	586	542/200	[22]/2006
SnO <sub>2</sub> nanoboxes			~ 156		570/40	[20]/2011
SnO <sub>2</sub> nanosheets	Hydrothermal	156	762	534/50	[19]/2012	
Fe <sub>2</sub> O <sub>3</sub> @SnO <sub>2</sub> nanorattles	Spray	200	865	419/30	[18]/2009	
Double-shelled SnO <sub>2</sub>		625	704	642/40	[17]/2013	
		3125	418	392/40		
SnO <sub>2</sub> @C	Lyophilization	200	978 (2nd)	1039/100	[9]/2012	
		1000	770			
		150	1314 (1st)	823/100	[8]/2012	
SWNTs@ SnO <sub>2</sub> @PPy	Lyophilization	1000		553/100		
		3000	480			
		500	1865 (1st)	1021/500	[7]/2013	
SnO <sub>2</sub> /graphene	Lyophilization	1000	994			
		10A	631			
		500		696/300	[5]/2012	
SnO <sub>2</sub> nanosheets	Hydrothermal	78.2		559/20	[4]/2010	





**Fig. 6.** TEM images of M-SGCs after 151 (a), 304 (b), and 475 (c) charge–discharge cycles at  $0.5 \text{ A g}^{-1}$ . (d) TEM image of SGCs after 147 charge–discharge cycles at  $0.5 \text{ A g}^{-1}$ .

M-SGCs, especially the high rate capability and long cyclic stability, is better than most of the  $\text{SnO}_2$ -based anodes ever reported, and can be a promising candidate for the next-generation of anode materials for high performance LIBs.

In order to explore the root of the excellent cycling stability of the M-SGCs, TEM images of M-SGCs after 151, 304, and 475 cycles of charge–discharge test at  $0.5 \text{ A g}^{-1}$  are obtained and compared in Fig. 6a–c. The TEM image (Fig. 6d) of SGCs after 147 charge–discharge cycles at  $0.5 \text{ A g}^{-1}$  is also presented for comparison. As shown in Fig. 6a,  $\text{SnO}_2$  nanocrystals are uniformly distributed on the rGO sheets, indicating that M-SGCs can maintain its structure after 151 cycles. After 304 charge–discharge cycles, the boundaries of  $\text{SnO}_2$  nanoparticles become blurry (Fig. 6b), suggesting that these particles tend to fuse together with repeated volume changes. But it is notable that, the surface of rGO sheets are enveloped with  $\text{SnO}_2$ , and the capacity of M-SGCs in the 304th cycle shows no fade. All these phenomena reveal that no  $\text{SnO}_2$  particles break away from rGO sheets, confirming the tight interaction between them. After 475 cycles, less  $\text{SnO}_2$  nanoparticles are observed on the surface of rGO sheets (Fig. 6c), indicating the electrode collapse. For SGCs, almost no  $\text{SnO}_2$  nanoparticles can be observed on rGO sheets only after 147 cycles (Fig. 6d), which suggests that the interaction between  $\text{SnO}_2$  nanoparticles and rGO sheets is very weak without the addition SDS during the synthesis process. This result reveals that SDS plays the key role to anchor  $\text{SnO}_2$  nanoparticles tightly on the surface of rGO sheets to improve the cycling life of the electrode materials.

The superior  $\text{Li}^+$  storage performance of M-SGCs including high reversible capacity, high rate capability and long cycling life may be attributed to the following benefits. (1) The monodispersion of  $\text{SnO}_2$  nanoparticles ensures the isolation of  $\text{SnO}_2$  nanoparticles and is beneficial for the suppression of their aggregation during electrochemical charge/discharge process, resulting in improved cycling stability. (2) The tight contact between  $\text{SnO}_2$  nanoparticles and rGO sheets can effectively anchor  $\text{SnO}_2$  nanocrystals on the

surface of rGO sheets, and thus prevents the aggregation of Sn nanoparticles and suppresses the mechanical loss of active materials in contact with the rGO sheets. (3) The guaranteed extremely small size of active materials can supply large specific surface area and abundant active sites for full utilization of active materials, and achieve high reversible conversion storage of  $\text{Li}^+$ . (4) Moreover, the initiate connection between  $\text{SnO}_2$  and rGO makes electron flowing from rGO sheets, which is famous for its good electronic conductivity and high surface areas, to the surface of  $\text{SnO}_2$  fast and smooth, leading to enhanced reversible capacity.

#### 4. Conclusions

In summary, with the aid of the binding molecule of SDS and the reducing agent of urea, small  $\text{SnO}_2$  nanoparticles have been controllably anchored on the flexible rGO support evenly and tightly for the formation of monodisperse  $\text{SnO}_2$ /rGO hybrid composites. Benefiting from the monodispersion of the nanosized  $\text{SnO}_2$  particles ( $\sim 5 \text{ nm}$ ), the highly conductivity and flexible mechanical property of rGO sheets, and the close interaction between  $\text{SnO}_2$  nanocrystals and rGO, the resultant M-SGCs deliver superior electrochemical performance in terms of cyclic stability and cycling life as well as rate capability for LIBs. Most importantly, this synthesis strategy, the desirable anchor of monodisperse  $\text{SnO}_2$  nanocrystals onto rGO sheets through a facile and friendly wet chemical route, is a versatile approach to promote the electrochemical performance of other metal oxides and can be scaled up easily for industrial production.

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## Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.jpowsour.2014.03.085>.

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